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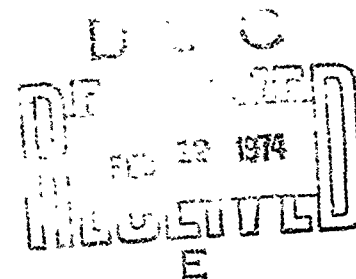
CARBORANE BURNING RATE CATALYSTS (Unclassified Title)

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Sacramento, California 95813

November 1973

Interim Technical Report for Period 1 February 1973 -  
15 August 1973

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Director of Science and Technology  
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## FOREWORD

This technical report, "Carborane Burning Rate Catalysts", was prepared as partial fulfillment of the requirements of Contract No. FO4611-71-C-0066 for the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was performed in the Propellant Development Department, Advanced Propellants Section of the Aerojet Solid Propulsion Company, Sacramento, California. This report, designated Aerojet Report No. 1840-26SA-2, records the results of work done during the interval 1 February 1973 to 15 August 1973. The program is monitored by Mr. N. VanderHyde.

Acknowledgement is made to Mr. N. VanderHyde of AFRPL and Mr. J. Braun and F. Pickett of NWC for their aid in selecting promising structures of new carborane burning rate catalysts. Acknowledgement is also made to Mr. R. F. Putman for the instrumental analyses performed on the new compounds, and Mr. T. S. Fletcher for propellant formulation and laboratory assistance.

This technical report has been reviewed and is approved.

FOR THE COMMANDER

Charles R. Cooke  
Chief, Solid Rocket Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  New carborane burning rate accelerators designed for use in solid propellants, without the problems associated with current accelerators, have been prepared. High molecular weight, non-volatile derivatives of bis-(1-carboranylmethyl) and bis-(1-carboranylethyl) ethers were synthesized and evaluated for compatibility in HTPB binders as well as compatibility and ballistic effects in aluminized HTPB propellants.  (Continued)		

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The branched unsaturated carborane derivative, 3,7-dimethyl-2,6-octa bis-(1-carboranylmethyl)ether, has proved to be compatible with cured HTPB at the 60% level. Propellants containing high levels of this carborane showed no evidence of plasticizer bleeding over long periods of storage. Also propellants containing this derivative have exhibited higher burning rates than those containing equivalent amounts of NHC.

Several alkyl oxygen ether derivatives of bis-(1-carboranylmethyl) ether have been prepared and partially evaluated. Both the butoxyethoxymethyl and isobutoxyethoxymethyl derivatives are more effective as burning rate accelerators than NHC. These materials, although compatible with cured HTPB at the 60% level, exude slightly from test propellants.

Two pentaborane carboranes were prepared and evaluated as propellant plasticizers. It was found that the small closo-carborane cage is highly susceptible to oxidative degradation and consequently of limited value as a burning rate accelerator.

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APPENDIX A - CARBORANE BURNING RATE CATALYSTS - SUMMARY

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I. INTRODUCTION (U)

(U) This is the second Interim Technical Report submitted in partial fulfillment of the requirements of Contract FO4611-71-C-0066. The technical portion of this report covers the period 1 February 1973 to 15 August 1973. This work is being performed in the Advanced Propellants Section of which Dr. R. L. Lou is Manager. Dr. L. J. Rosen is Technical Manager of the program and Dr. R. Fitzgerald is the Principal Investigator. A summary of the carboranes prepared during this reporting period is included as Appendix A.

II. OBJECTIVE (U)

(U) The objective of this program is to produce carborane burning rate catalysts which can be used in solid propellants and are (1) more efficient than currently available burning rate catalysts, and (2) free from problems associated with current catalysts.

(U) AFRPL personnel have devised a series of requirements for carborane catalysts which would be acceptable for advanced propellant application:

(U) A. Wide Liquid Range. An ideal compound would have a liquid range of from -65°F to 350°F if used as a plasticizer. Co-cured compounds may have a lesser liquid range.

(U) B. Low Vapor Pressure. The compound must have low volatility at temperatures up to 350°F if used as a plasticizer. Co-cured compounds should have low volatility up to 200°F.

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- (U) C. High Boron Content. Compounds should have a boron content comparable to or greater than that of NHC to assure a high catalytic effectiveness.
- (U) D. Minimal  $I_{sp}$  Loss. Compounds should cause little or no loss in  $I_{sp}$  when substituted for other binder ingredients in an aluminized composite formulation.
- (U) E. Processing Aid. If possible, the compound should act as a processing aid to improve solids loading capability. For this purpose a low viscosity compound is desired.
- (U) F. No Detrimental Effects on Binder Properties. Mechanical properties of propellant should not be adversely affected by the inclusion of the additives.
- (U) G. Non-Migrating. Compounds should be designed so their molecular structure precludes migration. This may be accomplished by bulky molecules or by co-curing with propellant binder.
- (U) H. Molecular Structure Flexibility. If possible, the basic molecule should be amenable to addition of various functionalities such as NCO, OH or COOH.
- (U) I. Thermal Stability. Compounds should not be subject to thermal degradation or decomposition at temperatures up to 350°F.
- (U) J. Chemically Stable. Compounds should not undergo oxidative degradation or chemical interaction with other propellant ingredients at storage or use conditions.

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(U) K. Non-Hazardous. Compounds should not be inherently sensitive nor should they sensitize propellants or propellant ingredients.

(U) L. Miscible with Binder. Neat compounds should be miscible with the binder(s) over a wide range of concentrations since the potential requirement for high catalyst levels exists.

(U) M. Efficient Production. The compounds should be amenable to high yield production from safe, simple reactions.

(U) Bis-(1-carboranylmethyl) ether was selected at the inception of the program as a baseline compound for the preparation of new catalysts. Several carborane compounds based on pentaborane were to be prepared, and evaluated as burning rate accelerators, in order to determine the stability of the small closo-carborane in propellant systems.

### III. SUMMARY (U)

(U) The following is a summary of progress made during the 6-1/2 month period 1 February 1973 to 15 August 1973.

### A. COMPOUNDS EVALUATED IN PROPELLANT SYSTEMS (U)

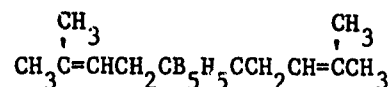
(U) The following compounds were evaluated in propellant systems during the current reporting period at either NWC or ASPG.

<u>Structure</u>	<u>Properties</u>
<p>3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranyl)methyl ether</p>	<p>mp <math>&lt; -10^{\circ}\text{C}</math> 46% boron</p>

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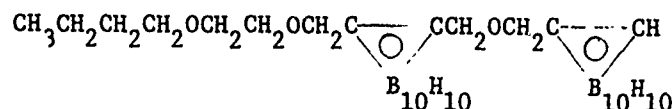
Structure



2,4-di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane

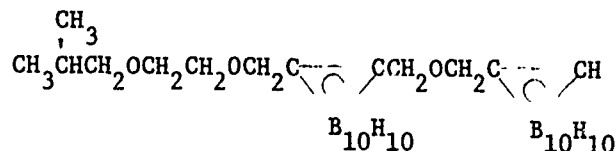
Properties

mp <-10°C  
24.6% boron  
bp 85-86/1 mm



mp <-10°C  
47.0% boron

2-Butoxyethoxymethyl-bis-(1-carboranylmethyl)ether



mp -10°C  
47.6 boron

2-Isobutoxyethoxymethyl-bis-(1-carboranylmethyl)ether

(U) The carborane evaluated at NWC, 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl)ether, was tested at the 5 and 8% level in an 86% solids, aluminized HTPB propellant containing 0.5 micron UFAP. All of the above carboranes were evaluated at ASPC at between 1 and 3% in an 87% solids HTPB propellant containing 3 micron UFAP.

1. 3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl)ether, GBCE (U)

(U) This alkylated bis-carborane was found to exhibit both a liquid range extending well below -10°C, and high compatibility with HTPB propellants. Also, from evaluations at NWC, propellant plasticized with this carborane gave higher burning rates than a control propellant plasticized with NHC at the same weight percent.

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2. 2,4-Di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane (U)

(U) This carborane was found to be completely miscible with uncured HTPB at ambient temperatures and compatible with the cured binder at the 60% level. Unfortunately, it was noted that exposure to an air atmosphere for an extended period of time, e.g. 5 to 10 days, resulted in a significant thickening of this material followed by formation of a white precipitate. It was also observed that cured propellant samples containing this carborane had extremely hard crust-like exterior surfaces. Burning rate data were not obtained with the pentaborane carborane.

3. 2-Butoxyethoxymethyl-bis-(1-carboranylmethyl)ether (U)

(U) This oxygen ether substituted carborane was found to be more efficient as a burning rate accelerator than either NHC or GBCE. Although this carborane is highly compatible with HTPB, plasticizer bleeding was observed from a cured propellant plasticized at the 8% level.

4. 2-Isobutoxyethoxymethyl-bis-(1-carboranylmethyl)ether (U)

(U) The isobutoxy functionalized carborane has not as yet been fully evaluated for compatibility with HTPB propellant systems. However, it has been found to provide higher burning rates in test propellants than GBCE.

B. OTHER COMPOUNDS (U)

(U) Numerous other carborane derivatives were prepared which tentatively do not meet the requirements of chemical stability, wide liquid range or HTPB compatibility. These compounds are listed in Table 1

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TABLE 1. MELTING POINTS AND COMPATIBILITY IN HTPB OF CARBORANE DERIVATIVES

Compound*	Melting Point, °C	Solubility** in Cured HTPB, %
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CB}_5\text{H}_5\text{CCH}_2\text{CH}=\text{CCH}_3 \\   \qquad \qquad   \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	<-10	>60
$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_2\text{C}=\text{CHCH}_2\text{CB}_5\text{H}_5\text{CH} \end{array}$	<-10	>60
$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3\text{C}=\text{CHCH}_2-\text{Z}-\text{CH}_2\text{CH}=\text{CCH}_3 \end{array}$	81-82	-
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{SCH}_2\text{Z}-\text{H} \end{array}$	<-10	>60
$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_2\text{C}=\text{CHCH}_2-\text{Z}-\text{H} \end{array}$	<-10	>60
$(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2\text{CH}=\text{CHCH}_2-\text{Z}-\text{H}$	<-10	-
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2-\text{Z}-\text{H}$	<-10	>60
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2-\text{Z}-\text{H} \end{array}$	-10	>60
$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\   \qquad   \qquad   \\ \text{CH}_2-\text{CH}_2-\text{CH}_2 \end{array} \text{CHCH}_2\text{OCH}_2-\text{Z}-\text{H}$	45-55	-
$\text{CH}_2=\text{CHCH}_2\text{C} \begin{array}{c} \diagup \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C} \begin{array}{c} \diagup \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCH}=\text{CH}_2^{***}$	<-10	>60
$\text{HCB}_{10}\text{F}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CH}$	25-30	~50
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{F}_{10}\text{CH} \end{array}$	<-10	-
<p>* <math display="block">\text{Z} = \begin{array}{c} \text{---C---CCH}_2\text{OCH}_2\text{C---C---} \\   \qquad \qquad   \\ \text{B}_{10}\text{H}_{10} \qquad \text{B}_{10}\text{H}_{10} \end{array}</math></p>		

\*\* R-45M/IPDI-Plasticizer cured 72 hours at 140°F

\*\*\* Average structure, note technical discussion

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along with their melting points and, where determined, solubilities in cured HTPB binder. Candidate compounds are included for comparison.

### IV. TECHNICAL DISCUSSION (U)

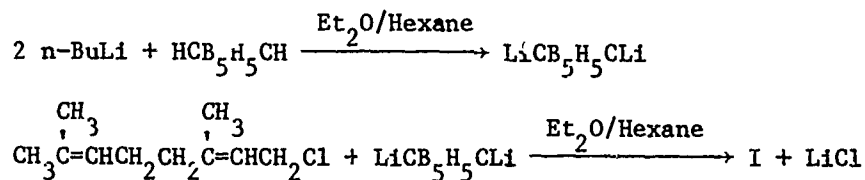
#### A. COMPOUND SYNTHESIS (U)

##### 1. Preparation of Pentaborane Carboranes (U)

(U) Since the chemical and physical properties of pentaborane carboranes are not well known, two closo-carboranes were prepared in order to carry out investigations on the stability and compatibility of the small carborane unit.

##### a. 3,7-Dimethyl-2,6-octadienyl-2,4-dicarba-closo-heptaborane (I)\* (U)

(U) This mono-alkylated carborane derivative was prepared on a small scale (~2g) through treatment of dilithio-2,4-dicarba-closo-heptaborane with one equivalent of 1-chloro-3,7-dimethyl-2,6-octadiene.



The resulting product was purified by solid-liquid chromatography and identified via its spectral (NMR and IR) properties. Due to the small quantity of this material, no further characterization of physical properties was attempted.

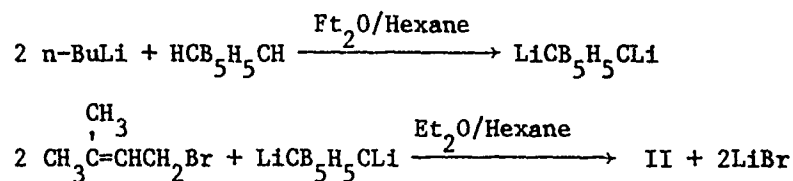
\* For simplicity, compounds reported here will be numbered as in the Program Outline, February 1973. Those carboranes, which had not been previously numbered, will be numbered as reported in the sixteenth through twenty-second Monthly R&D Status Reports.

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## b. 2,4-Di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane (II) (U)

(U)

The dilithio derivative of 2,4-dicarba-closo-hepta - borane was prepared through treatment of the small carborane with n-butyllithium in mixed ether-hexane solvent. This transformation requires approximately 20 hours for completion. The dilithio salt was then treated with two equivalents of isopentenyl bromide and the reaction mixture stirred vigorously while boiling under reflux for 10 hours.



Normal workup procedures, including product purification via chromatography and distillation, resulted in a 65% yield of clear liquid; bp 85-86/1mm.

Analysis of this material by glpc indicated a purity of greater than 99%.

## 2. Preparation of bis-(1-carboranylmethyl)ether derivatives (U)

### a. Alkenyl Derivatives (U)

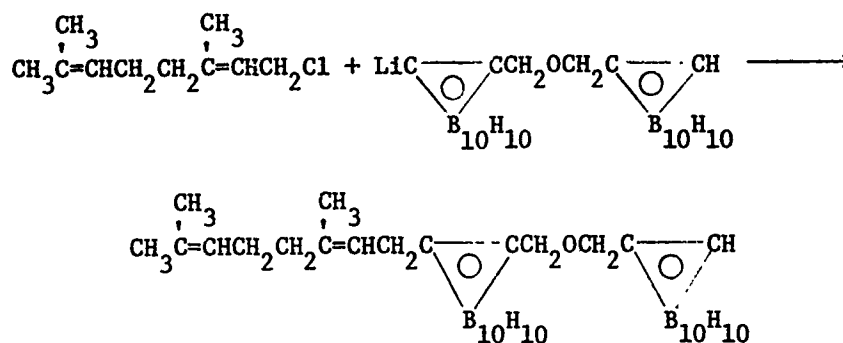
(U)

Alkenyl, or unsaturated, substituents, are most effective to date at reducing the melting point of bis-(1-carboranylmethyl)ether derivatives. Substituents containing branching as well as unsaturation are particularly effective at increasing liquid range and HTPB compatibility of bis-carboranes.

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- (1) 3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranyl-methyl)ether (VI) (U)

(U) The derivative, VI, was prepared in the usual manner from geranyl chloride and the monolithium derivative of the baseline bis-(1-carboranylmethyl)ether.



VI

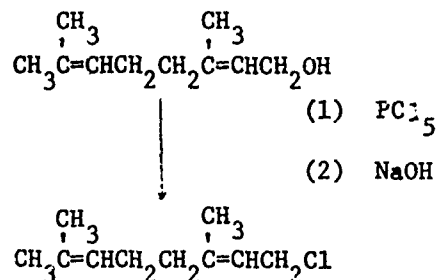
After purification by column chromatography, VI was obtained as a clear liquid melting below -10°C and boiling above 150°C (0.1mm).

(U) Preparation of the geranyl chloride starting material was altered significantly from that procedure reported in the first Interim Technical Report. It was found, through several small scale preparations, that treatment of geranyl alcohol with phosphorus pentachloride in hydrocarbon solvents, followed by aqueous workup under basic conditions, provided an alternate route for the synthesis of 1-chloro-3,7-dimethyl-2,6-octadiene.\*

\* Often referred to by the common name "geranyl chloride".

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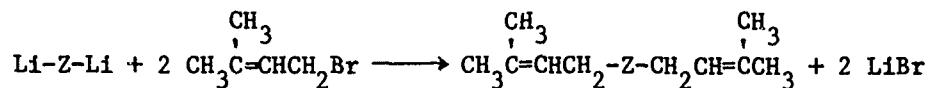
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This procedure provided the alkyl chloride in higher yields than the previously reported method. More significantly, the cost per gram of the alkylating agent is reduced by at least a factor of five. Also, large scale preparations of this material are more amenable to the phosphorus pentachloride procedure.

(2) Di-(3-methyl-2-butene)-bis-(1-carboranylmethyl) ether (XII) (U)

(U) Compound XII was synthesized, on a small scale, due to its ease of preparation and chemical similarity to 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether. This synthesis was accomplished



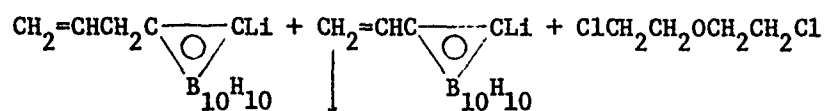
in high yield (>80%) through treatment of dilithio-bis-(1-carboranylmethyl) ether with excess isopentenyl bromide. The fact that the material is a solid melting at approximately 81°C, although unfortunate, further strengthens the theory that symmetrical carboranes tend to have much higher melting points than their unsymmetrical isomers.

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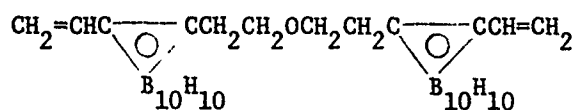
(3) Mixture of Allyl- and vinyl-bis-(1-carboranylethyl) ethers (XVII) (U)

(U) Although XVII is an accurate description, in respect to boron content, of the carboranes formed through this sequence,

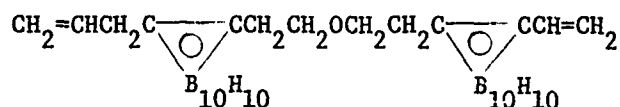


XVII + 2 LiCl

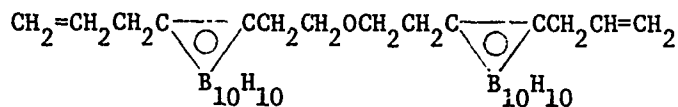
the actual mixture is composed of three products (shown below) in the ratio of a:b:c of 1:2:1.



XVII-a



XVII-b



XVII-c

As expected, the product mixture is compatible with HTPB and exhibits a liquid range extending below  $-10^\circ\text{C}$ .

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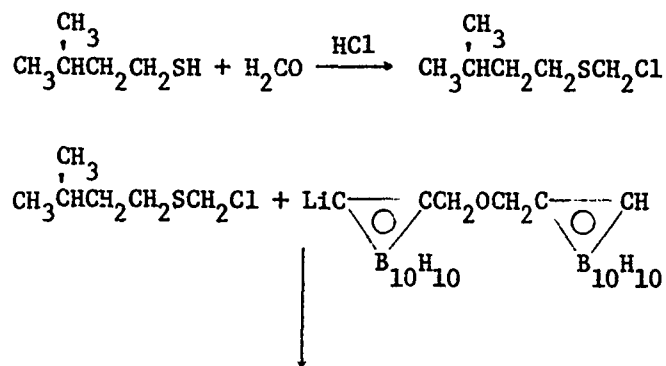
(U) The starting materials for this particular mixture were not prepared at ASPC, but were previously obtained from Olin Chemical Company. It is not intended that large quantities of the final products be prepared in this manner, but enough will be synthesized in order to complete evaluations as burning rate accelerators. Should promising results be obtained, the starting allyl and vinyl carboranes will be obtained through treatment of the corresponding alkynes with decarborane.

## b. Thio Derivative (U)

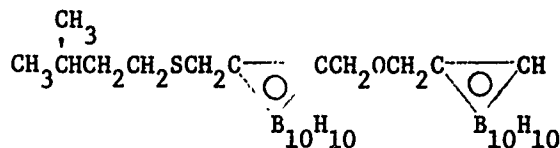
### (1) Isopentylthiomethylene-bis-(1-carboranylmethyl) ether (XIII) (U)

(U) Isopentyl chloromethyl sulfide, required for the synthesis of XIII, is prepared through treatment of isopentylmercaptan with formaldehyde under acidic aqueous conditions. The product chloromethyl sulfide is isolated, in approximately 65% yields, through distillation and characterized via its NMR and IR spectra. This material was found to be greater than 95% pure through glpc analysis.

(U) On reacting lithio-bis-(1-carboranylmethyl) ether with the above described chloromethyl sulfide, a low yield of liquid product is obtained after normal workup procedures.



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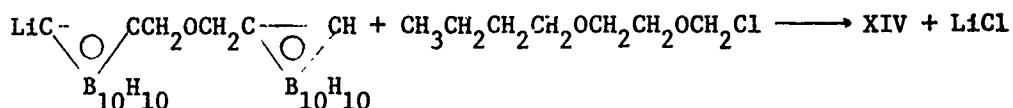
(XIII)

The IR spectrum of this material is in agreement with the assigned structure. However, the NMR spectrum indicates that more than a single product is formed. The absorption assigned to the methylene hydrogens on the carbon situated between the carborane and sulfur groups does not appear as the expected singlet at approximately  $\delta 3.26$  (as observed in CMES), but as three different apparent singlets within this general area. It is likely, therefore, that an alternate reaction is competing with the normal substitution pathway. If, for example, an  $\alpha$ -elimination type mechanism is the competing reaction, both low yields and several products could be readily explained.

c. Oxygen Ether Derivatives (U)

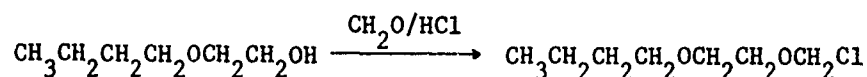
- (1) 2-Butoxyethoxymethyl-bis-(1-carboranylmethyl) ether (XIV) (U)

(U) Carborane XIV was prepared through treatment of lithio-bis-(1-carboranylmethyl)ether with 2-butoxyethyl chloromethyl ether.



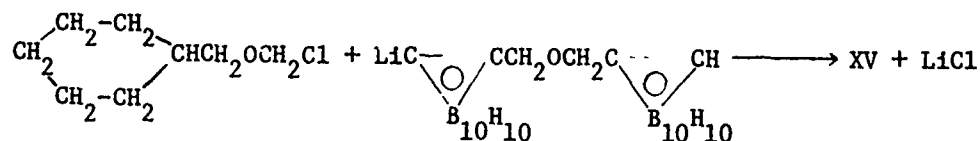
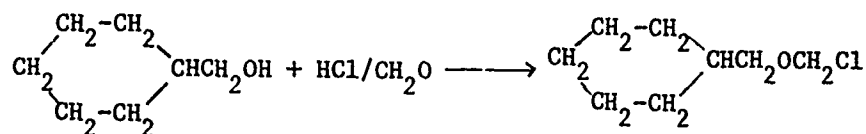
Product purification and characterization were accomplished through well established techniques. The chloromethyl ether used in this preparation was synthesized from the parent alcohol via treatment with aqueous hydrochloric acid and paraformaldehyde.

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## (2) Cyclohexylmethyl [bis-(1-carboranylmethyl)ether] methyl ether (XV) (U)

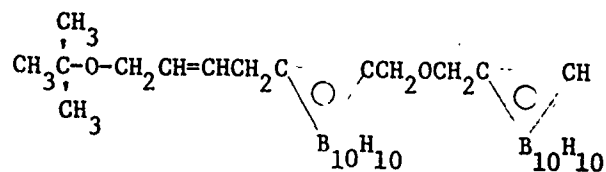
(U) The preparation, purification and identification of carborane XV were all accomplished through analogous procedures used on carborane XIV.



Unfortunately, the purified carborane crystallized on standing at room temperature for several days.

## (3) 4-t-Butoxy-2-butenyl-bis-(1-carboranylmethyl) ether (XV) (U)

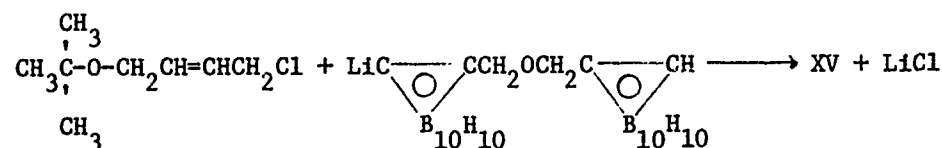
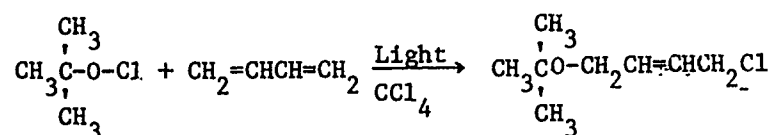
(U) The oxygen ether derivatized carborane, 4-t-butoxy-2-butenyl-bis-(1-carboranylmethyl) ether XV,



XV

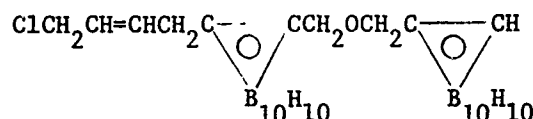
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which contains both unsaturation and branching was synthesized through a two step-reaction sequence.



The preparation of 4-t-butoxy-1-chloro-2-butene was accomplished through treatment of 1,3-butadiene with tert-butyl hypochlorite in carbon tetrachloride solvent. On irradiation with a 200-watt light globe, the reaction is initiated and proceeds smoothly at 0°C. The allylic chloride product was purified by distillation and identified via its spectral properties.

(U) Treatment of this halide with lithio-bis-(1-carboranylmethyl)ether gave two isolated products. The minor one was identified as the desired carborane, while the major product appeared to be derived from substitution of the t-butoxy function yielding 4-chloro-2-butenyl-bis-(1-carboranylmethyl)ether (below).



This material was tentatively identified from its NMR spectrum. The low yields observed in the preparation of carborane XV make this compound an unlikely candidate for a burning rate accelerator.

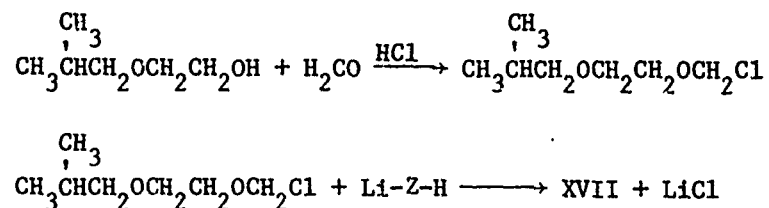
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(4) 2-Isobutoxyethoxymethyl-bis-(1-carboranylmethyl) ether (XX) (U)

(U) A branched oxygen ether substituted carborane was prepared using procedures similar to those used in the synthesis of carboranes XIV and XV.

(U) Isobutoxyethyl chloromethyl ether, required for the synthesis of carborane XX, was prepared through treatment of the parent alcohol with paraformaldehyde and hydrochloric acid. Alkylation of lithio-bis-(1-carboranylmethyl)ether with this chloride gave the desired product.



Carborane XX, on purification by column chromatography, was found to be a clear liquid melting below  $-10^\circ\text{C}$  and boiling above  $150^\circ\text{C}/1\text{mm}$ .

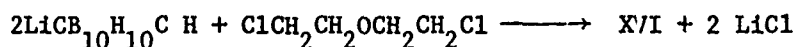
3. Preparation of meta-bis-(1-carboranylethyl)ethers (U)

(U) Several carborane derivatives based on meta-carborane were prepared in anticipation of providing carborane plasticizers which exhibit high compatibility with HTPB. Also, the use of carboranylethyl ether was incorporated into these compounds in order to obtain low liquid ranges.

a. Meta-bis-(1-carboranylethyl)ether (XVI) (U)

(U) Carborane XVI was synthesized in high yields via the reaction of mono-lithio-meta-carborane with bis-chloroethyl ether.

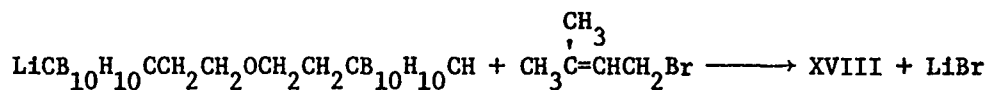
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Purification of this carborane, accomplished through column chromatography, yielded a white wax-like material which melted below 30°C. The low melting point observed for this baseline material indicates (as shown below) that only slight modifications will be necessary in order to attain a liquid range extending below -10°C.

## b. Isopentenyl-meta-bis-(1-carboranylethyl)ether (XVIII) (U)

(U) The preparation of this plasticizer was accomplished through treatment of lithio-meta-bis-(1-carboranylethyl)ether with one equivalent of isopentenyl bromide.

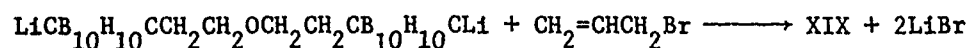


On normal work up and chromatographic purification, less than a 30% yield of product is realized from this step. Although the product yield is low, the physical characteristics of this carborane are encouraging, as the material is much less viscous than alkylated bis-(1-carboranylmethyl)ethers. This could be a result of either the ethyl ether function or the use of meta-carborane.

## c. Diallyl-meta-bis-(1-carboranylethyl)ether XIX (U)

(U) A dialkylated meta-carborane derivative was prepared via the reaction of dilithio-meta-bis-(1-carboranylethyl)ether with excess allyl bromide.

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The product carborane, XIX, was also a very fluid liquid, but again less than a 30% product yield was realized from the alkylation reaction.

(U) These low yields from seemingly straight forward reactions are most likely due to secondary reaction of the baseline meta-carborane with butyl lithium. For example, if treatment of bis-(1-carboranyl-ethyl)ether with an alkyl lithium reagent resulted in partial cleavage of the ether function rather than formation of the lithiocarborane, low yields would be expected. Should this be the case, it would be desirable to synthesize these compounds through a different reaction sequence (note recommendations).

#### B. STABILITY EVALUATIONS ON PENTABORANE CARBORANES (U)

(U) Small samples of 3,7-dimethyl-2,6-octadienyl-2,4-dicarba-closo-heptaborane (I) and 2,4-di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane II were placed in sealed ampules at ambient temperature under several atmospheric conditions. These included: (1) anhydrous oxygen; (2) anhydrous nitrogen; (3) anhydrous air; and (4) nitrogen saturated with water.

(U) The effects of the various conditions on both carboranes can be summarized very simply, in that, all samples in contact with oxygen gradually thickened and a white precipitate formed. Samples under moist or anhydrous nitrogen showed no visual or analytical (glpc analysis) evidence of change.

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(U) An infrared analysis of those samples, shown below (Figure 1), subjected to an oxygen atmosphere indicated gradual formation of boric oxide type materials (eq. broad absorptions at  $1450\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$ ). The carbonyl hydrogen and boron hydrogen stretching frequencies (C-H,  $2980\text{ cm}^{-1}$  and B-H,  $2600\text{ cm}^{-1}$ ) appear to remain constant in intensities, relative to each other, throughout the oxidative decomposition. This would indicate the carborane cage itself, rather than the alkyl substituents, is being oxidized.

(U) The observed oxidative instability of 2,4-dicarba-closo-heptaboranes has discouraged further work on these materials.

### C. COMPATIBILITY STUDIES (U)

(U) The compatibility of bis-carborane plasticizers was determined in HTPB binders and propellants. Binder compatibility studies were performed at ASPC and propellant evaluations were conducted both at ASPC and the Naval Weapons Center, China Lake, California.

#### 1. Compatibility in HTPB Binders (U)

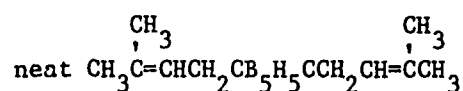
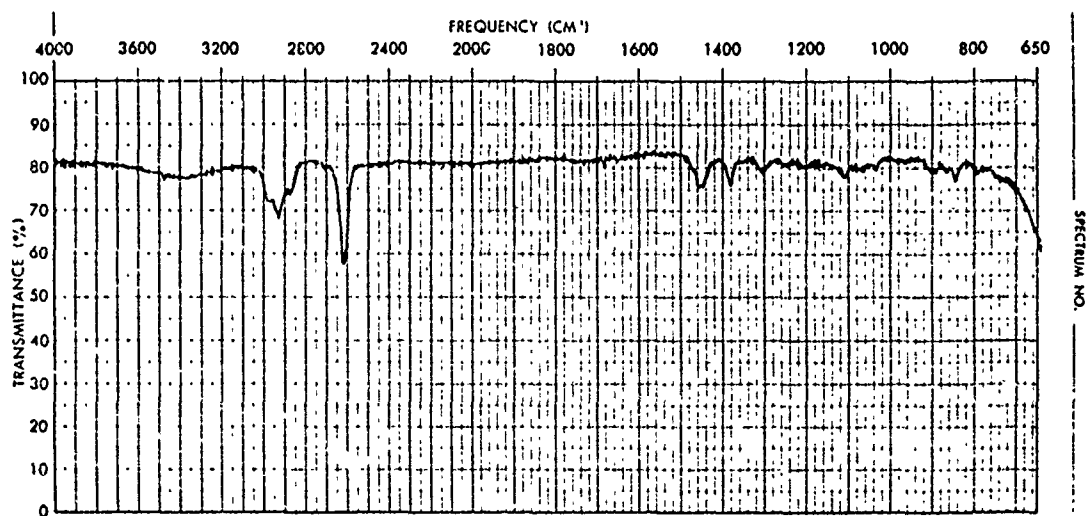
(U) The compatibility of several carborane plasticizers in cured R-45M was determined by mixing specified amounts of plasticizer with a stoichiometric blend of R-45M and IPDI.\* The samples, 2 gram, were mixed thoroughly, degassed for 20 minutes at ambient temperature and then cured thoroughly for 72 hours at  $140^{\circ}\text{F}$ .

(U) Those carborane compounds evaluated in this manner, were all compatible in the cured binder at the 60% level. The plasticizers evaluated are shown in Figure 2.

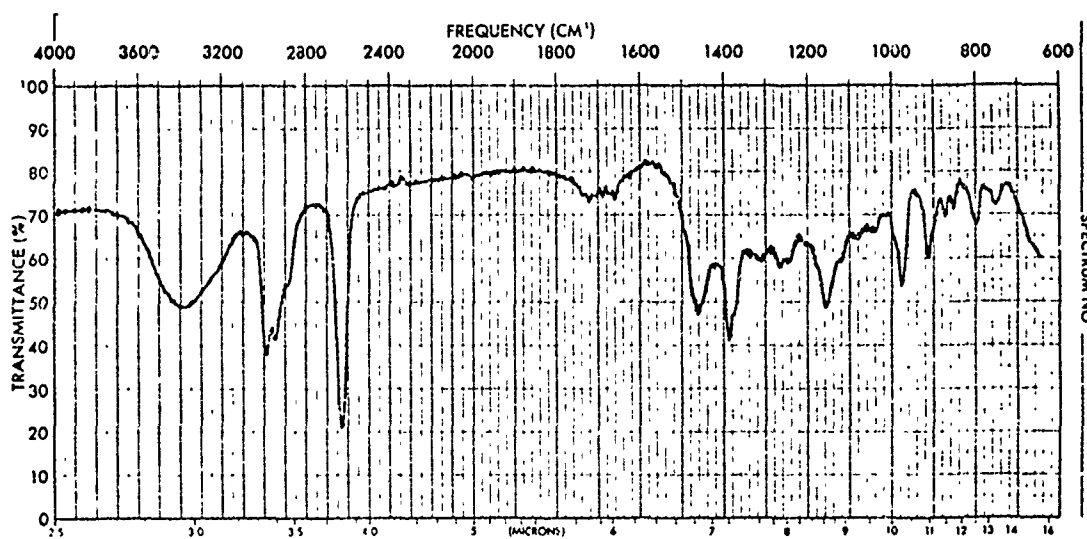
\* Isophoronediiisocyanate

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Carborane II

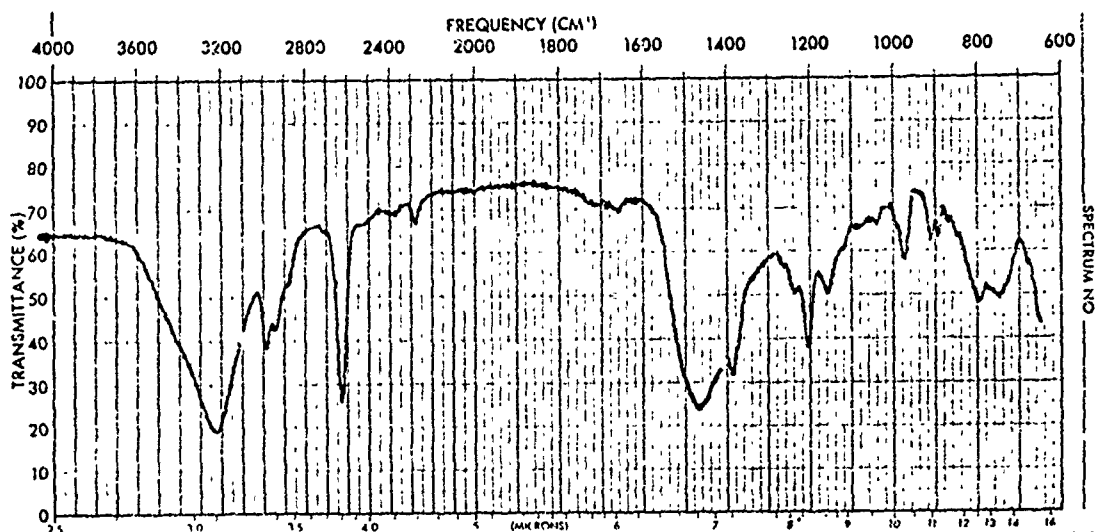


After 48 hours under an O<sub>2</sub> Atmosphere

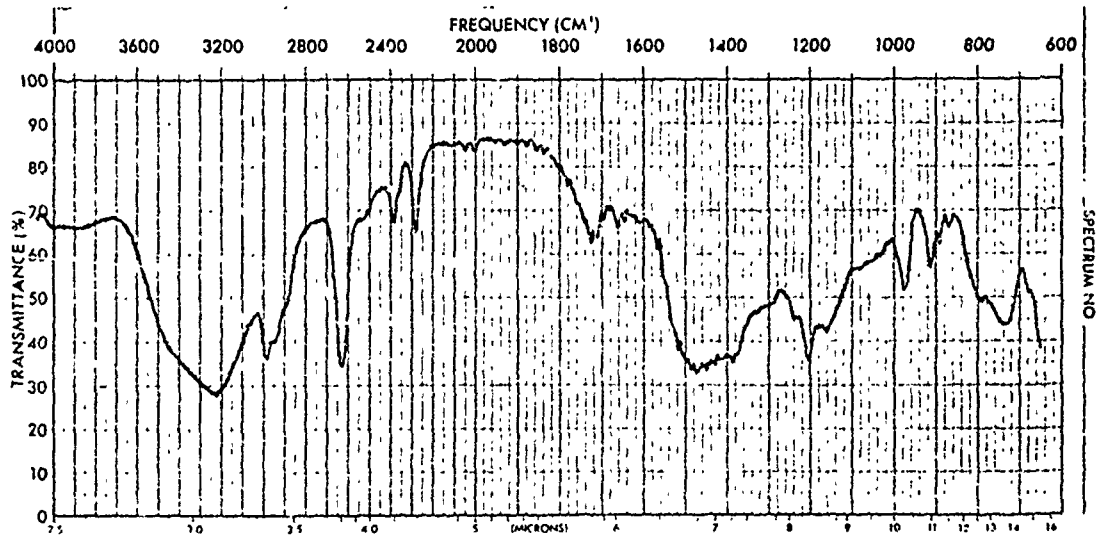
Figure 1. Infra Spectra of Carborane II on Exposure to an Oxygen Atmosphere

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200 hours under an O<sub>2</sub> atmosphere



400 hours under an O<sub>2</sub> atmosphere

Figure 1. Infra Spectra of Carborane II on Exposure to an Oxygen Atmosphere (Cont.)

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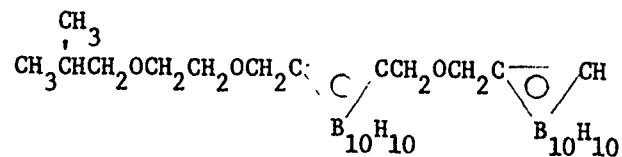
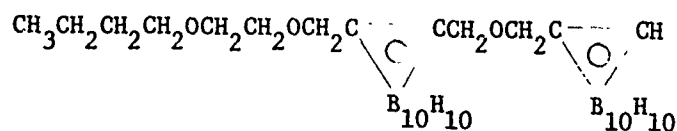
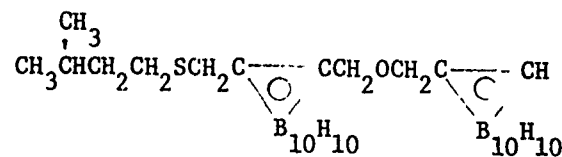
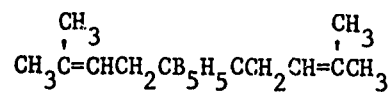


Figure 2. Carboranes Evaluated for HTPB Compatibility\*

\* These compounds were all found to be soluble in R-45M at equal to or greater than the 60% level.

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### 2. Compatibility in HTPB Propellants (U)

(C) The 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether (GBCE) was evaluated at NWC for compatibility at the 5 and 8% level in an 86% solids aluminized propellant containing 0.5 micron UFAP. The propellants were mixed, cast and cured for seven days at 140°F. At the end of the cure cycle no evidence of plasticizer bleeding was observed at these levels. Investigations are currently being conducted on the migration tendencies of GBCE as compared to NHC.

(C) The isobutoxyethoxymethyl- and butoxyethoxymethyl-bis-carboranes were evaluated at ASPC at the 8% level in an 86% solids propellant. With both plasticizers, on curing, the propellant surface remained dry for approximately one week at ambient temperature with no apparent plasticizer bleeding. After this initial period, a light film of liquid appeared on the top surface of the propellant cube. It can be concluded that these carborane derivatives are only marginally compatible with HTPB propellant at the 8% level.

(C) Carborane II, 2,4-di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane, was incorporated in a standard 86 wt% solids, HTPB propellant at the 9.6% level. Propellant cubes, on curing at 135°F for 24 hours, exhibited hard crust-like exterior surfaces, indicating a chemical surface reaction was taking place rapidly at this temperature. Consequently, this propellant was considered a potential safety hazard and was disposed of.

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### D. PROPELLANT EVALUATION (U)

#### 1. Selection of Propellant Formulation (U)

(U) Several propellant formulations were prepared and characterized by burning rates and hazard properties. The objective of this study was to obtain a formulation which when plasticized with low percentages of 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether would exhibit a burning rate of approximately 1.5 ips at 1000 psi. The results of this investigation are shown in Table 2.

(C) These data dramatically illustrate the increased effectiveness of carborane burning rate accelerators as the oxidizer particle size is reduced. This study delineates a practical approach to the achievement of burning rates in the range of 1.5 to 2.0 ips using but 1 to 3% carborane and without submicron oxidizer. The 87% solids propellant containing 3 $\mu$  AP, which exhibited a burning rate of 2.45 ips at 1000 psi with 3% carborane, was adopted as a baseline formulation for evaluations of carborane burning rate accelerators.

#### 2. Efficiency of Carborane Burning Rate Accelerators (U)

(C) In order to determine the lowest concentration of GBCE required in the baseline formulation to obtain a burning rate of approximately 1.5 ips at 1000 psi, propellants plasticized at the 1 and 2% level were prepared and evaluated. Also, several new carborane plasticizers were evaluated in this formulation at the 2% level. These results along with a comparison to a NHC plasticized baseline propellant are shown below (Table 3).

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TABLE 3. SAFETY DATA AND BURNING RATES FOR HTPB-CARBORANE PROPELLANTS (U)

Carborane	<u>1% GBCE</u>	<u>2% GBCE</u>		
	Burning Rates (ips)			
1000 psi	1.51	1.87		
2000 psi	2.30	2.88		
	Safety Data			
	Cured	Uncured	Cured	Uncured
Rotary Friction, g	2330	1920	3560	1800
Impact, cm/2 kg	13.3	29.0	12.2	18.0
Onset of Exotherm, °F	435	480	-	471
Carborane 2%	<u>Butoxyethoxymethyl-*</u>	<u>Isobutoxyethoxymethyl-*</u>		
	Burning Rates (ips)			
1000 psi	2.00	2.32		
2000 psi	3.00	3.67		
	Safety Data			
	Cured	Uncured	Cured	Uncured
Rotary Friction, g	1950	1150	1500	2420
Impact, cm/2 kg	5.7	14.9	13.6	23.4
Onset of Exotherm, °F	-	472	-	484
Carborane 2%	<u>Allyl/Vinyl Mixture**</u>	<u>NHC</u>		
	Burning Rates (ips)			
1000 psi	1.93	1.83		
2000 psi	2.94	2.90		
	Safety Data			
	Cured	Uncured	Cured	Uncured
Rotary Friction, g	650	430	1450	>4000
Impact, cm/2 kg	6.7	9.0	17.4	11.2
Onset of Exotherm, °F	-	431	-	411

\* indicates substituted bis-(1-carboranylmethyl)ether

\*\* allyl/vinyl mixture of bis-(1-carboranylethyl)ethers

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(C) From the results in Table 3, it can be seen that several bis-carborane compounds have been prepared which are near equal or more efficient than NHC. Although both butoxyethoxymethyl- and isobutoxyethoxymethyl-bis-(1-carboranylmethyl)ethers are more effective burning rate accelerators than NHC, the observations that when used at high concentration these plasticizers tend to exude from the cured propellant somewhat limits the value of these carboranes. On the other hand, GBCE has exhibited high compatibility with HTPB propellant systems and further evaluations of this material are currently in progress. The allyl/vinyl mixture of bis-(1-carboranylethyl)ethers has not as yet been evaluated for compatibility with HTPB propellants.

### V. EXPERIMENTAL SECTION (U)

(U) Those syntheses which have been previously reported (First Interim Technical Report, October 1972) will not be reported in detail here.

#### A. 1-Chloro-3,7-dimethyl-2,6-octadiene (U)

(U) A rapidly stirred slurry of phosphorous pentachloride (55.0g, 0.30 mole) in 100 ml of hexane was cooled (ice-water bath), and 30.8g (0.20 mole) of 3,7-dimethyl-2,6-octadien-1-ol in 75 ml of hexane was added dropwise. The reaction mixture was then heated at reflux for 0.5 hr, allowed to equilibrate to ambient temperature, then hydrolyzed with 500g of ice. The organic layer from the resulting two phase mixture was separated, washed with saturated sodium chloride solution (3x100 ml) and dried ( $\text{MgSO}_4$ ). This solution was concentrated by rotary evaporation and distilled at reduced pressure yielding 22g (64%) of 1-chloro-3,7-dimethyl-2,6-octadiene: bp  $63-66^\circ\text{C}/0.5 \text{ mm}$  (reported bp  $64-65^\circ\text{C}/0.05 \text{ mm}$ ).<sup>1</sup>

<sup>1</sup> G. Stork, P. A. Grieco and M. Gregson, Tetrahedron Lett., 1393 (1969).

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B. 2-Butoxyethyl chloromethyl ether (U)

(U) The following is a representative procedure for the syntheses of several chloromethyl alkyl ethers and chloromethyl isopentyl sulfide. Spectral and physical properties of these compounds are listed individually below.

(U) To a stirred mixture of 7.5g (0.25 mole) of paraformaldehyde and 50 ml of benzene was added 100 ml of concentrated hydrochloric acid over a 10 min period. The resulting two phase mixture was heated to 30°, and treated dropwise with 23.6g (0.20 mole) of 2-butoxyethanol over a 0.5 hr period. On heating to 50°C, the reaction mixture was stirred for 2 hours, cooled, and the layers separated. The upper organic layer was washed with water (1x200 ml), dried ( $\text{MgSO}_4$ ) and concentrated by rotary evaporation. Distillation of the concentrate at reduced pressure gave 2-butoxyethyl chloromethyl ether: bp 56-59°C/1 mm; ir (neat) 2870 and 2960 ( $\text{CH}_2$ ) and 1120  $\text{cm}^{-1}$  (C-O); nmr  $\delta$  0.90 (t, 3,  $\text{CH}_3$ ), 1.22 to 1.63 (m broad, 4, C- $\text{CH}_2$ ), 3.27 to 3.88 (m, 6,  $\text{CH}_2$ -O), and 5.51 ppm (s, 2,  $-\text{CH}_2\text{Cl}$ ).

C. 2-Isobutoxyethyl chloromethyl ether (U)

(U) Prepared as described above; bp 59-61°C/2 mm; ir (neat) 2890-2960 ( $\text{CH}_2$ ) and 1120  $\text{cm}^{-1}$  (C-O); nmr  $\delta$  0.88 (d, 6,  $J = 8$  Hz,  $\text{CH}_3$ ), 1.84 (m, 1, C-H), 3.20 (d, 2,  $J = 8$  Hz,  $\text{CHCH}_2\text{O}$ ), 3.47 to 3.88 (m, 4,  $\text{OCH}_2\text{CH}_2\text{O}$ ), and 5.47 ppm (s, 2,  $\text{CH}_2\text{Cl}$ ).

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D. Cyclohexylmethyl chloromethyl ether (U)

(U) Prepared as described above: bp 39-42/2 mm;  $\delta$  0.90 to 1.92 (m, 11, ring), 3.40 (d, 2,  $J=7\text{Hz}$ ,  $\text{C}-\underline{\text{CH}_2}\text{O}$ ) and 5.45 ppm (s, 2,  $\underline{\text{CH}_2}\text{Cl}$ ).

E. Isopentyl chloromethyl sulfide (U)

(U) Prepared as described above: bp 60-63/3 mm; nmr  $\delta$  0.94 (d, 6,  $J=7\text{Hz}$ ,  $\underline{\text{CH}_3}$ ), 1.55 (m, 3, methylene), 2.69 (m, 2,  $\text{C}-\underline{\text{CH}_2}-\text{S}$ ), and 4.68 ppm (s, 2,  $\underline{\text{CH}_2}\text{Cl}$ ).

F. 4-t-Butoxy-1-chloro-2-butene (U)

(U) To a solution of 400 ml of carbon tetrachloride and 150 ml of 1,3-butadiene was added 21g (0.20 mole) of freshly distilled t-butyl hypochlorite. The reaction mixture, maintained under an oxygen free nitrogen atmosphere, was cooled in an ice-water bath; and irradiated with a 200-watt frosted light bulb for 0.5 hr. During this period the solution changed from light yellow to colorless, indicating the disappearance of t-butyl hypochlorite. Concentration of this mixture followed by distillation at reduce pressure gave 17.0g (53%) of 4-t-butoxy-1-chloro-2-butene: bp 68-72°C/10 mm;  $n_D^{25}$  1.4530, (lit<sup>2</sup> bp 69-72°C/10 mm;  $n_D^{25}$  1.4526).

G. 2,4-Di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane (U)

(U) The following procedure is representative for both pentaborane carboranes prepared. Into 250 ml of diethyl ether/hexane solvent (2.5/1), under a dry nitrogen atmosphere, was added 10.0g (0.118 mole) of 2,4-dicarba-closo-heptaborane. The reaction mixture was cooled to -30°C then treated with butyl lithium (0.240 mole as a 15% solution in hexane). On equilibration

2 J. K. Kochi, J. Amer. Chem. Soc., 84, 2785 (1962).

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to ambient temperature the mixture was stirred for 18 hours during which time the dilithio-carborane separates from the solvent as a fine suspension. With rapid stirring, this heterogeneous mixture was treated with 50g (excess) of isopentenyl bromide, then boiled at gentle reflux for 10 hours. The mixture was then quenched with 200 ml of water and the layers separated. The upper organic layer was washed with saturated sodium chloride solution (2x200 ml), dried ( $\text{MgSO}_4$ ) and concentrated by rotary evaporation. Distillation of the residue gave 17.0g (65%) of 2,4-di-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane: bp 85-86°C/1 mm; ir 2930 (C-H), 2620 (B-H) and 1660  $\text{cm}^{-1}$  (C=C), nmr  $\delta$  1.69 (s, 6,  $\text{CH}_3$ ), 1.75 (s, 6,  $\text{CH}_3$ ), 3.19 (d, 4,  $\text{J}=8\text{Hz}$ ,  $\text{CH}_2$ ), and 5.34 ppm (2, 2,  $\text{J}=8\text{Hz}$ , =CH).

#### H. Alkyl bis-(1-carboranylmethyl)ether (U)

(U) The following is a representative procedure for the synthesis of a series of alkenyl, alkyl ether and alkyl sulfide substituted carboranes. A solution of 5.0g (0.015 mole) of bis-(1-carboranylmethyl) ether in 60 ml of anhydrous diethyl ether, under a nitrogen atmosphere, was cooled (ice-water bath) and treated with butyl lithium (0.016 mole as a 15% solution in hexane) while maintaining a temperature of between 10 and 20°C. The ethereal solution was then allowed to equilibrate to ambient temperature and 7.5g (0.045 mole) of 2-butoxyethyl chloromethyl ether was added by syringe. The reaction mixture was then boiled at gentle reflux ( $\sim 38^\circ\text{C}$ ) for 15 hours. On cooling, 50 ml of 5% hydrochloric acid was added and the organic layer from the resulting two-phase mixture was separated, washed

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with saturated sodium chloride solution (3x100 ml) and dried ( $\text{MgSO}_4$ ). This mixture was concentrated by distillation at reduced pressure to an oily residue. The residue was dissolved in a minimum amount of hexane and eluted through a silica gel column (25x200 mm) with hexane solvent. Concentration of the eluent yielded 4.9g (71%) of clear liquid 2-butoxyethoxymethyl-bis-(1-carboranylmethyl)ether: mp  $<-10^\circ\text{C}$ , ir (neat) 2880 and 2950 ( $\text{CH}_2$ ), 2600 (B-H) and 1140  $\text{cm}^{-1}$  (C-O).

(U) Other carborane compounds prepared by this procedure are listed in Table 4 along with their yields. The NMR and IR spectra of these compounds were consistent with their proposed structures.

TABLE 4. SUBSTITUTED BIS-(1-CARBORANYLMETHYL) AND BIS-(1-CARBORANYLETHYL)ETHERS

<u>Carborane</u>	<u>% Yield</u>
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{-Z-H} \end{array}$	65
$(\text{CH}_3)_3\text{COCH}_2\text{CH=CHCH}_2\text{-Z-H}$	18
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{SCH}_2\text{-Z-H} \end{array}$	20
$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad \quad   \\ \text{CH}_3\text{C=CHCH}_2\text{-Z-CH}_2\text{CH=CCH}_3 \end{array}$	85
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C=CHCH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CH} \end{array}$	22
$\text{CH}_2=\text{CHCH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH=CH}_2$	26

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I. Meta-bis-(1-carboranylethyl)ether (U)

(U) To a solution of meta-carborane (5.0g, 0.035 mole) in 50 ml of diethyl ether was added butyl lithium (0.037 mole as a 15% solution in hexane) while maintaining a temperature of between 10 and 20°C. The mixture was allowed to equilibrate to ambient temperature then (2.5g 0.018 mole) of bis chloroethyl ether was added dropwise. After the addition, the solution was heated to gentle reflux for 15 hours, cooled, and treated with 50 ml of water. The resulting two phase mixture was separated, and the upper organic layer washed with saturated sodium chloride solution (2x100 mm), dried ( $\text{MgSO}_4$ ) and concentrated to a wax-like residue by rotary evaporation. This material was eluted through a silica gel column (25x200 mm) with hexane to yield, on concentration of eluents, 5.1g (82%) of meta-bis-(1-carboranylethyl)ether: mp 25-30°C; nmr  $\delta$  2.13 (t, 4,  $J=7\text{Hz}$ ,  $\text{CH}_2$ ), 2.81 (s (broad), 2, C-H) and 3.29 ppm (t, 4,  $J=7\text{Hz}$ ,  $\text{CH}_2\text{-O}$ ). Derivatives of this compound, prepared via the procedure described in part H above, are listed with yields in Table IV.

J. Mixture of Allyl- and Vinyl-bis-(1-carboranylethyl)ethers (U)

(U) This carborane mixture was prepared using the procedure described above for meta-bis-(1-carboranylethyl)ether. The allyl and vinylcarborane starting materials were obtained from Olin Chemical Co. as a 50/50 mixture. Thus, for stoichiometric purposes, a molecular weight of 177g was assigned this mixture. An 83% yield of the mixed allyl- and vinyl-bis-(1-carboranylethyl) ethers was realized from this procedure which had: bp >200°C/2 mm; mp <-10°C; ir 2900 and 2960 ( $\text{CH}_2$ ), 2600 (B-H) and 1140  $\text{cm}^{-1}$  (C-O).

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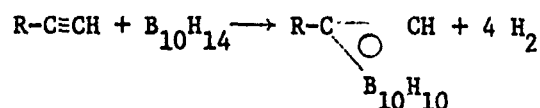
## VI. CONCLUSIONS AND RECOMMENDATIONS (U)

### A. CONCLUSIONS (U)

- (U) 1. Pentaborane carboranes are of little value as solid propellant ingredients due to their oxidative instability.
- (U) 2. Unsaturated and branched-unsaturated substituents are effective at increasing the liquid range of the bis-carboranes, as well as providing derivatives with improved compatibility in HTPB binders.
- (U) 3. Oxygen ether derivatives of bis-(1-carboranylmethyl)ether are efficient burning rate accelerators, but of marginal value at high concentrations due to migratory tendencies in HTPB propellants.
- (U) 4. The use of ortho- and meta-bis-(1-carboranylethyl)ethers as baseline carboranes, allows the synthesis of new carborane compounds which exhibit low liquid ranges and high compatibility with HTPB.

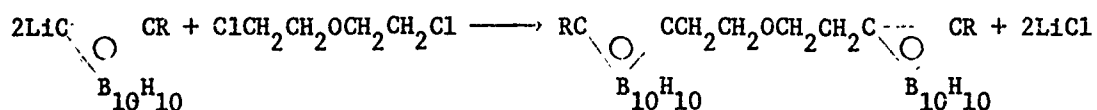
### B. RECOMMENDATIONS (U)

- (U) 1. The 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether (GBCE) should be fully evaluated in R-45M propellants in order to determine the processability, effectiveness, and stability of this material.
- (U) 2. Work should continue on the preparation of dialkyl-bis-(1-carboranylethyl)ethers. A logical pathway for the large scale preparation of these compounds would be, first, the synthesis of an alkylated carborane through treatment of the desired alkyne with decarborane



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followed by conversion to the lithio-carborane and reaction with bis-chloroethyl ether.



(U) 3. Efforts should be directed towards the syntheses of selected isomeric ortho and meta carborane burning rate accelerators. Evaluation of these materials will provide an indication as to whether the additional effort involved in the preparation of the meta carboranes is warranted.

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**Appendix A**

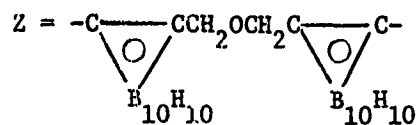
**CARBORANE BURNING RATE CATALYSTS**

**SUMMARY**

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## INDEX



1.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CB}_{10}\text{H}_5\text{CCH}_2\text{CH}=\text{CCH}_3 \\ | \\ \text{CH}_3 \end{array}$
2.  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_2\text{C}=\text{CHCH}_2\text{CB}_{10}\text{H}_5\text{CH} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
3.  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{---Z---CH}_2\text{CH}=\text{CCH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
4.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{SCH}_2\text{---Z---H} \\ | \\ \text{CH}_3 \end{array}$
5.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{---Z---H}$
6.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{---Z---H} \\ | \\ \text{CH}_3 \end{array}$
7.  $(\text{CH}_3)_3\text{COCH}_2\text{CH}=\text{CHCH}_2\text{---Z---H}$
8.  $\begin{array}{c} \text{CH}_2\text{---CH}_2\text{---CH} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{---CH}_2 \end{array} \text{CHCH}_2\text{OCH}_2\text{---Z---H}$
9.  $\text{HCB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CH}$
10.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{C}=\text{CHCH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CH} \\ | \\ \text{CH}_3 \end{array}$
11.  $\text{CH}_2=\text{CHCH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}^-\text{B}_{10}\text{H}_{10}\text{CCH}_2\text{CH}=\text{CH}_2$
12.  $\text{CH}_2=\text{CHCH}_2\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCH}=\text{CH}_2 \text{ (mixture)}$

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2,4-DI-(3-methyl-2-butene)-2,4-dicarba-closo-heptaborane

Physical Properties

1. Clear liquid, bp 85-86°C/1 mm
2. Boron content, 24.6%

Characterization

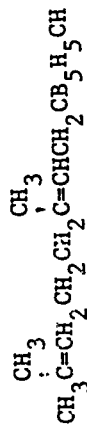
1. IR and NMR spectra are consistent with the assigned structure.

Comments - This carborane is readily available from the parent pentaborane carborane. In an air atmosphere this material undergoes oxidative decomposition.

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3, 7-Dimethyl-2, 6-octadienyl-2, 4-dicarba-closo-heptaborane

Physical Properties

1. Clear liquid, mp  $<-10^\circ\text{C}$
2. Boron content, 24.6%

Characterization

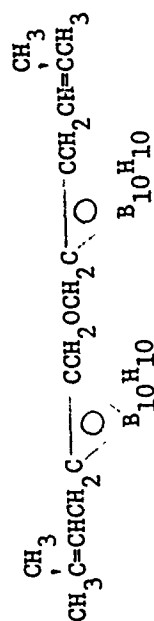
IR and NMR spectra are consistent with the assigned structure

Comments - This material rapidly decomposed in the presence of oxygen.

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Di-(3-methyl-2-butene)-bis-(1-carboranylmethyl) ether

Physical Properties

1. Crystalline solid, mp 81°C
2. Boron content, 46.3%

Characterization

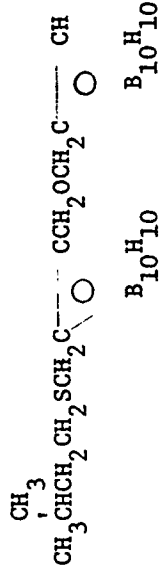
1. The NMR spectrum is consistent with the assigned structure

Comments - Due to the high melting point, this material was not evaluated further as a burning rate accelerator.

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Isopentylthiomethylene-bis-(1-carboranylmethyl) ether

Physical Properties

1. Liquid, mp  $<-10^\circ\text{C}$
2. Boron content, 48.5%

Characterization

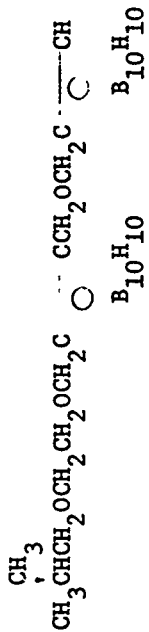
1. The IR spectrum is consistent with the assigned structure.

Comments - This material was not prepared in sufficient yield or purity to be considered a potential propellant plasticizer.

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Isobutoxyethoxymethyl-bis-(1-carboranylmethyl) ether

Physical Properties

1. Viscous liquid
2. Boron content, 47.0%

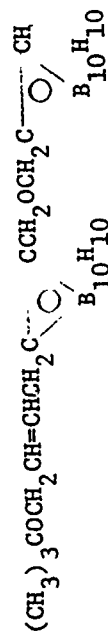
Characterization

1. IR and NMR spectra are consistent with the assigned structure.

Comments - This carborane exudes slightly from propellant plasticized at the 8% level.

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4-t-Butoxy-2-butenyl-bis-(1-carboranylmethyl)ether

Physical Properties

1. Liquid, mp <-10°C
2. Boron content, 47.4%

Characterization

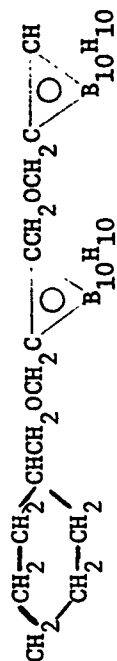
1. IR and NMR spectra are consistent with the assigned structure

Comments - The synthesis of this material was carried out in very low yield.

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Cyclohexylmethyl [bis-(1-carboranyl-methyl) ether] methyl ether

Physical Properties

1. Crystalline solid, mp 45-55°C
2. Boron content, 47.4%

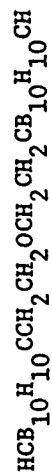
Characterization

1. The NMR spectrum is consistent with the assigned structure.

Comments - Compatibility evaluations have not been carried out on this compound.

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Meta-bis-(1-carboranylethyl) ether

## Physical Properties

1. White wax-like material, mp  $<30^{\circ}\text{C}$
2. Boron content, 60.4%

## Characterization

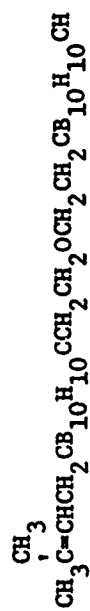
1. The NMR spectrum is consistent with the assigned structure

Comments - This carborane is a synthetic intermediate for plasticizers based on an ethyl ether and meta-carborane.

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Isopentenyl-meta-bis-(1-carboranylethyl) ether

Physical Properties

1. Liquid, mp  $< -10^\circ\text{C}$
2. Bp  $> 200^\circ\text{C}/1\text{mm}$
3. Boron content, 50.7%

Characterization

1. IR and NMR spectra are consistent with the assigned structure.

Comments - This carborane is highly compatible with HTPB.

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Diallyl-meta-bis-(1-carboranylethyl)ether

Physical Properties

1. Fluid liquid, mp  $<-10^\circ\text{C}$
2. Boron content, 49.3%

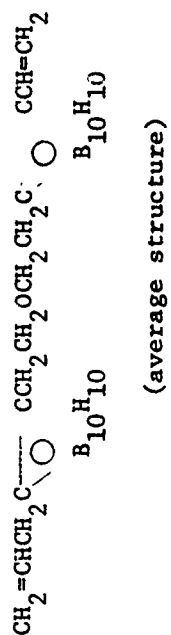
Characterization

1. IR and NMR spectra are consistent with the assigned structure.

Comments - Compatibility evaluations have not, as yet, been carried out on this carborane.

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Mixture of allyl- and vinyl-bis-(1-carboranylethyl)ethers

Physical Properties

1. Liquid, mp < -10°C
2. Boron content,

Characterization

1. The IR spectrum is consistent with the assigned structure.

Comments - This mixture of allyl and vinyl substituted carboranyl ethers is miscible with HTPB.

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GLOSSARY

AFRPL	Air Force Rocket Propulsion Laboratory
ASPC	Aerojet Solid Propulsion Company
CMES	Carboranylmethyl ethyl sulfide
DTA	Differential thermoanalysis
GBCE	3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether
glpc	Gas liquid partition chromatography
HTPB	Hydroxy terminated polybutadiene
Hz	Hertz
IPDI	Isophoronediiisocyanate
IR, ir	Infrared
I <sub>sp</sub>	Theoretical specific impulse
m	Multiplet
NHC	n-Hexyl carborane
NMR, nmr	Nuclear magnetic resonance
NWC	Naval Weapons Center
PPM	Parts per million
R-45M	Hydroxy terminated polybutadiene
s	Singlet
t	Triplet
UFAP	Ultrafine ammonium perchlorate

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(this page is unclassified)